



Laboratoire PPSM – UMR CNRS 8531

Photochimie et Photophysique Supramoléculaires et Macromoléculaires

Soutenance de thèse au PPSM

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Auditorium D. Chemla (bâtiment de l'institut d'Alembert)

Qing Zhou

Directeur de thèse : Fabien Miomandre

«Synthesis of new tetrazines functionalized with photoactive and electroactive groups»

In this thesis, we have prepared different types of *s*-tetrazine derivatives which are electroactive and fluorescent.

In the first chapter, we discuss the literature published on the synthesis and properties of *s*-tetrazines. The second chapter is devoted to the study of ions pair receptor containing *s*-tetrazine. Their design is quite simple since they are bis-*s*-tetrazine derivatives linked by polyethylene oxide chains of various lengths. The receptors interact with ion pairs through anion- π interactions which have seldom been observed in solution. The formation of a complex between the ammonium salt ($C_8H_{17}NH_3^+ \cdot Br^-$ and $C_8H_{17}NH_3^+ \cdot I^-$) and *s*-tetrazine receptors is demonstrated by NMR titration experiments. It is also proved by NMR and fluorescence titrations that one receptor containing a pentaethylene oxide chain binds stronger to ammonium salt than its shorter equivalents. Furthermore, they display a selectivity for halides in the order $I^- > Br^- > Cl^-$. During the course of the titration a photoinduced reaction producing I_2 or Br_2 was detected. We proposed a mechanism for this side reaction from the UV-vis. absorption, NMR and fluorescence titrations data.

In the third chapter, various *s*-tetrazines derivatives with different types of substituents have been prepared in order to better understand and control the physico-chemical properties of the *s*-tetrazine ring. It was found that the electrochemical and fluorescence properties depend solely on the electron affinity of the substituent and not on its size. For example, electron donor groups quench the fluorescence of *s*-tetrazine even if they are not directly linked. A new family of *s*-tetrazines derivatives has been obtained through an unexpected reactivity of chloro-*s*-tetrazine with *n*-butyl lithium. This reaction gave unsymmetrical *s*-tetrazines bearing one heteroatom and one alkyl chain which will be useful for future applications.

The last part deals with original *s*-tetrazines dyads. These compounds are very bright thanks to an energy transfer from a donor moiety (naphthalimide or benzimidazole) to *s*-tetrazine. Besides its excellent fluorescence properties, one compound owns two stable and independent anion-radicals. Combination of these two properties was used in a device that electrochemically and reversibly switch on an off the fluorescence.

PPSM

ENS Cachan – 61 avenue du Président Wilson
94235 Cachan Cedex – France

Tél : +33 1 47 40 53 38 – Fax : +33 1 47 40 24 54

e-mail : ahusson@ppsm.ens-cachan.fr

site web : <http://www.ppsm.ens-cachan.fr>

